UTILIZATION OF WASTE

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REGENERATION OF SLIME GENERATED IN CHEMICAL POLISHING OF LEAD CRYSTAL

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A technology for regeneration of chemical pickling waste resulting from crystal glass has been developed, which makes it possible not only to solve the environment-related problems of contamination of ambient medium but also to decrease the consumption of red lead. The complex lead-containing material obtained in the study can find wide application in the synthesis of low-melting glasses and vitreous coatings.

The social significance of environmental problems is currently growing and the possibilities of finding solutions for these problems are expanding. We find it unacceptable when factories producing lead crystal keep dumping slime generated in chemical polishing. Considering that the weight of articles in acid polishing decreases by approximately 6 – 10%, one can easily imagine the scope of such waste. A rational solution for this problem is urgently needed.

Crystal glassware is polished by treatment in a mixture of hydrofluoric and sulfuric acids. While the surface layer of glass dissolves, the metal cations, primarily lead, potassium, and sodium cations, form lead sulfates and alkaline hexafluorosilicates, which sink. To achieve a high-quality polished surface, these difficultly soluble suspended salts have to be periodically removed from the pickling bath. Otherwise they may cover parts of the product surface and prevent the effect of acids, which leads to formation of defects [1].

It is known that factories producing crystal glass neutralize acid pickling waste by means of milk of lime. In this case the mixture of hydrofluoric and sulfuric acids transforms into nontoxic salts insoluble in water, i.e., calcium fluoride (fluoric feldspar) and calcium sulfate (gypsum), which are solid components [2]. Pickling slime without detoxication is carried to waste deposits, where its acid component penetrates into soil, contaminates subsurface waters, and causes irreparable damage to the ambient environment [3].

Some important environmental laws, namely "On the Protection of Atmospheric Air" and "On industrial waste," which have been adopted in the Russian Federation in 1998 – 1999, postulated the basic principles of state policy and state administration. These principles include protection of human health, preservation and restoration of favorable environmental conditions, and preservation of natural resources [4]. In the context of these regulations the problem discussed here appears extremely topical and has to be solved, which implies not only detoxication but also regeneration of pickling slime for the purpose of using it in the production of lead crystal. Regeneration of precipitates has to meet the following requirements:

– pickling precipitate has to be transformed into a lead compound suitable for crystal production;

– the lead compound should have a sufficient degree of purity and stability of chemical composition;

– the process has to be simple and environmentally clean.

The waste used in the experiments was pickling bath precipitate from the Dyat'kovskii Khrustal' JSC, which is a dirty-white paste of relative moisture 50 – 55% and pH = 0.5 – 0.6. By multiple rinsing the pH level of the filtrate was brought up to 4.5 – 5.0. The precipitate after washing and drying (pickling precipitate) constitutes white powder of bulk density 2600 kg/m^3 and specific surface area 120 m^2/kg. According to the x-ray (Fig. 1) and chemical analysis data, the pickling precipitate contains lead sulfate (over 50 %) and potassium and sodium hexafluorosilicates (up to 30%).

It is known that lead sulfate is virtually insoluble in water and diluted acids but dissolves fairly easily in concentrated alkali solutions. Potassium and sodium hexafluorosilicates are difficultly soluble compounds, which under the effect of alkalis transform into soluble silicates and fluorides. Since lead carbonate is a compound suitable for crystal glass production, it was decided to regenerate the pickling precipi-

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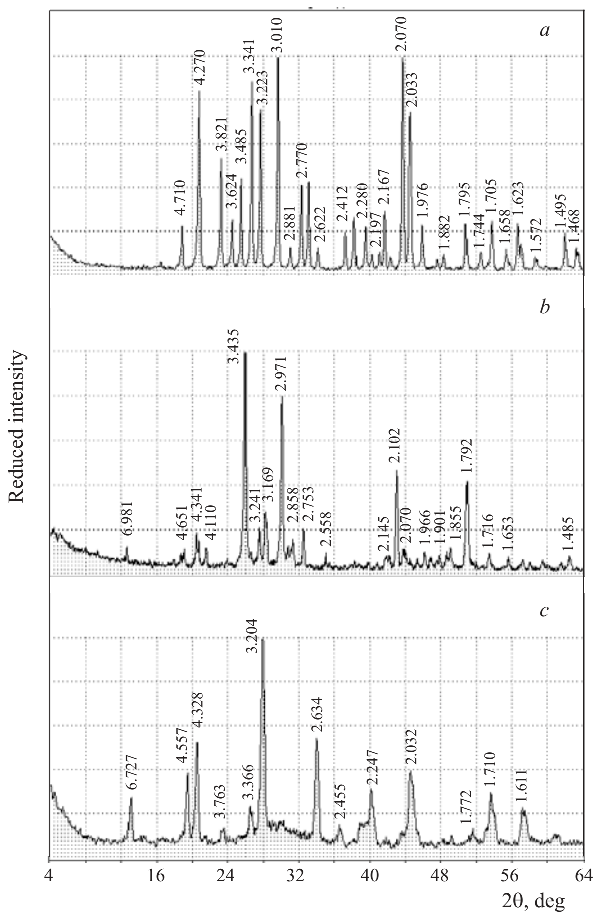

Fig. 1. Diffraction patterns of initial picking precipitates (*a*), product of regeneration containing lead sulfide (*b*), and complex lead-bearing material (*c*).

tate by means of an alkaline solution of sodium carbonate in corresponding temperature-time conditions.

Lead sulfate in the course of regeneration reacts with carbonate and hydroxide and produces base lead carbonate and soluble sulfates. Alkaline hexafluoric silicates are hydrolyzed and form soluble silicates and fluorides. The silicates are in equilibrium with silicic acid gel, which precipitates. The above processes can be represented by the following reactions:

$$3PbSO_4 + 2Na_2CO_3 + 2NaOH \rightarrow Pb(OH)_2 \cdot 2PbCO_3\downarrow + 3Na_2SO_4;$$

$$Na_2SiF_6 + 6H_2O \rightarrow Na_2SiO_3 + 6NaF + 3H_2O;$$

$$K_2SiF_6 + 6H_2O \rightarrow K_2SiO_3 + 6KF + 3H_2O;$$

$$Na_2SiO_3 + (n + 1)H_2O \rightarrow SiO_2 \cdot nH_2O\downarrow + 2NaOH.$$

Thus, a suspension of base lead carbonate and silica gel is formed in the solution containing sulfates, fluorides, and silicates. The precipitate is filtered and washed in water.

Lead oxide and most of the lead compounds are currently categorized as danger class I; its maximum permissible concentration in air in a work zone should not exceed 0.01 mg/m^3 [5]. The product of regeneration obtained in our experiments, in our opinion, has no contraindications for use in glass melting. This is a complex material suitable for producing lead-bearing glasses (complex lead-bearing material abbreviated as CLM) and its application in production makes it possible to save up to 10% red lead consumed in production.

The dried CLM is white powder with bulk density 1780 kg/m^3 and specific surface area of 720 m^2/kg. According to the x-ray phase analysis data, its phase composition is represented by compound $NaPb_2(CO_3)_2(OH)$ or $2PbCO_3 \cdot NaOH$ (Fig. 1*c*). Analysis of chemical composition indicates that the material contains up to 70% lead oxide.

The procedure developed for obtaining CLM is simple and can be easily implemented in industrial conditions with minimal expenses. As a consequence of numerous laboratory experiments in the regeneration of pickling precipitate, a product with suitable chemicophysical properties and chemical composition was obtained. However, deviation from the optimum technological parameters can yield undesirable results, in particular, the formation of lead sulfide in the regeneration product (Fig. 1*b*). We have developed a reliable procedure making it possible to avoid the formation of PbS in the composite.

Thus a simple and reliable method for regeneration of pickling precipitate generated in the production of crystal glass can be reliably implemented with minimum cost in plants engaged in the chemical polishing of crystal.

A series of experiments was carried out to test the possibility of replacing lead in crystal production by the CLM. In estimating an appropriate quantity of the product of regeneration to replace red lead, it was taken into account that chemical polishing of articles removes up to 10 wt.% glass from the product surface. Consequently, The maximum quantity of lead that can be regenerated from the pickling waste should be sufficient for producing about 10% new glass. However, the maximum part of the CLM replacing red lead in experimental batches was 50%, since it was necessary, first, to disprove any deterioration of glass quality in using the CLM and on the other hand, to identify The maximum possible replacement part.

The batch formulas were calculated for glass with the following chemical composition (wt.%) 58 SiO_2, 1 B_2O_3, 1 ZnO, 24 PbO, 1 Na_2O, and 15 K_2O. Melting was performed in oxidizing conditions in a laboratory electric resistance furnace with silicon carbide heaters in corundum crucibles of 150 ml capacity at a temperature of 1400°C. The experiments revealed that the quality of glass remains high up to introducing 30% CLM. Even multiple repetition of the glass $\leftrightarrow$ melt cycle did not impair the quality of samples. Introduction of over 30% CLM caused a certain turbidity in the glass, possibly due to the effect of small quantities of fluorine contained in the regenerated product. It was found that

introducing from 10 to 30% facilitates a stable technological process and production of high-quality articles.

At the same time, the CLM can be effectively used as the main lead-bearing material in the production of low-melting enamels and glazes [6, 7]. The chemical composition of the CLM ensures vitrification of its melt virtually without any additional ingredients; accordingly, it can be taken as the basic composition. The physicochemical and technological properties of glasses based on the CCM can be modified within a wide range by introducing additional materials.

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